Vibration-Transit Theory for Time Correlation Functions in Liquids: A Model for Transits

Giulia De Lorenzi-Venneri and
Duane Wallace, T-1

Great progress has been done in the last two decades on the understanding of liquids, both experimentally [1] and theoretically [2]. The theory developed in T-1, recently given the name of "Vibration-Transit" theory, contributes to this field by providing a Hamiltonian formulation of the dynamics in liquids, so that properties can be readily calculated from first principles, within controllable levels of approximations. After a number of successful results from the theory, we have now applied it to time correlation functions and in particular to the evaluation of the dynamic structure factor $S(q,\omega)$.

Vibration-Transit theory is based on the idea that a liquid system moves on its potential energy surface by performing almost instantaneous jumps, or transits, between valleys. The theory postulates that the dominant majority of visited valleys are all random in structure (see Fig. 1) and that they are all equivalent in energy and vibrational properties. Vibrations and transits are the building blocks of liquid dynamics. The zeroth order approximation to the Hamiltonian expresses the liquid motion in terms of normal mode vibrations in a single infinitely extended harmonic random valley and can be explicitly calculated from first principles for actual systems. On the other hand, the nature and microscopic details of transits are still an open problem.

The vibrational motion gives a very good account of the equilibrium thermodynamics of monatomic elemental liquids at melt [3]. This was obtained by V-T theory without adjustable parameters, a result that no other tractable theory has yet achieved.

When extended to nonequilibrium properties, namely to time correlation functions [4], V-T theory implies that both contributions, vibrations and transits, must be explicitly taken into account. Again without adjustable parameters, the vibrational contribution to any time correlation function [e.g., $F_{vib}(q,t)$, the density-density autocorrelation function] can be calculated from the zeroth order Hamiltonian. In particular for the dynamic structure factor $S(q,\omega)$—the Fourier transform of $F(q,t)$—the vibrational contribution is the sum of independent scattering cross sections from the normal modes. $S(q,\omega)$ is particularly interesting because it is measured in inelastic scattering experiments. For the case of liquid sodium it was found that it is this vibrational contribution that determines not only a natural width for the Brillouin peak [5], but also it locates the position of its maximum, as shown in Fig. 2. The figure proves that this dispersion curve for the liquid (which is in agreement also with experiments) can be completely evaluated from only the independent vibrational modes in a single valley, without the need to invoke coupling between the modes and relaxation times, a notion in contrast with previous interpretations.

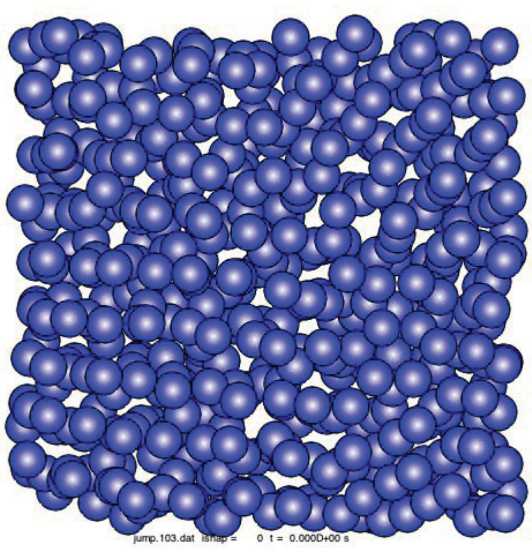

Fig. 1.
Typical random atomic structure in a liquid.

The major effect of transits, for which an explicit evaluation is not yet available, is to disrupt correlations within the normal mode vibrational motion and provide an additional source of inelastic scattering. We developed a model for the contribution of transits to inelastic scattering [6]. The model was developed for F(q,t). It was built in the spirit of Zwanzig's model for the velocity autocorrelation function, but we kept in mind the specific role played by transits in the decay of time correlation functions. It has three parameters and gives F(q,t) as:

$F_{liq}(q,t) = F_{Rayleigh} + F_{Brillouin}$

$= C(q)\, F_{vib}(q,\infty)\, \exp(-\alpha_1(q)t) + [F_{vib}(q,t) - F_{vib}(q,\infty)]\ \exp(-\alpha_2(q)t),$

where $F_{vib}(q,t)$ is determined by the vibrational contribution and $F_{vib}(q,\infty)$ expresses purely elastic scattering and gives rise to the elastic peak $F(q,\infty)\,\delta(\omega)$ in $S(q,\omega)$. Of the three parameters of the model, C(q) models the additional inelastic scattering due to transits, while $\alpha_1(q)$ and $\alpha_2(q)$ model the decorrelation due to transits, and are close to the mean single-atom transit rate. In $S(q,\omega)$ the effect of transits is to broaden the elastic Rayleigh peak and to broaden but not shift the Brillouin peak. We have shown that this model is capable of accurately reproducing the molecular dynamics (MD) results for $S(q,\omega)$ for liquid sodium (see Fig. 3), thus providing a new interpretation of the scattering process in terms of independent scattering events due to the normal vibrational modes and transits.

Work to study the role of transits and how to incorporate them in explicit evaluations within V-T theory is presently underway.

For more information contact Giulia De Lorenzi-Venneri at gvenneri@lanl.gov.

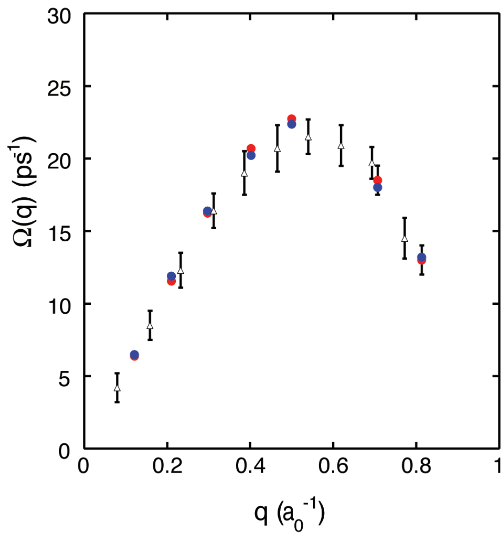

Fig. 2.
Dispersion curve for the Brillouin peak of inelastic scattering in liquid sodium at 395K. The position of the Brillouin peak maximum as a function of q is reported. V-T theory (blue circles) and MD simulation (red circles) almost coincide and also agree with x-ray experiments by Scopigno et al. [1] (triangles with error bars).

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Funding Acknowledgements
NNSA's Advanced Simulation and Computing (ASC), Weapons Supported Research.

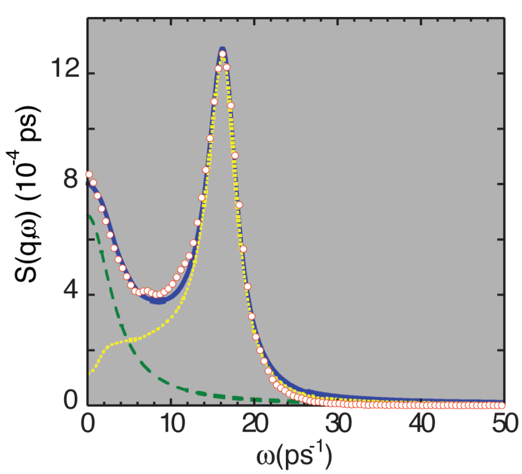

Fig. 3.
Dynamic structure factor for liquid sodium at 395K from V-T theory (blue solid line) and MD simulation (red circles). The V-T theory result is composed of two parts: the Brillouin peak (yellow dotted line), whose exact location and natural width are determined by vibrations, and whose width has a small contribution from transits, and the Rayleigh peak (green broken line), which is instead determined by transits. The vibrational contribution is evaluated within V-T theory, from a first principles Hamiltonian, while the transit contribution, for which an exact evaluation is not yet available, is modeled with a three-parameter relaxation function fitted to the MD results.